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We examined surface damage for polyvinyl chloride (PVC) sample after 260 minutes at an unmonochromated Al Kα X-ray source power at 600 W, because PVC decomposes very quickly due to the X-ray irradiation. The pendant Cl groups of the PVC were estimated to cleave more rapidly than C-C bonds in the main chains from two-center bond energies calculated by AM1 method using the model pentamer. The valence XPS of the polymer at the initial time, and after 120 and 260 minutes of X-ray irradiation were analyzed by deMon density-functional theory (DFT) calculations using the model pentamer. The simulated results afforded us that the pendant Cl groups of PVC cleave mainly due to the X-ray radiation.

Introduction

Since Beamson and Briggs [1] demonstrated that polymer materials exhibit a wide range of damage rate during XPS analysis, a considerable large number of investigators showed that the irradiation may lead to several types of the decomposition of polymers, poly(tetrafluoroethylene) (PTFE) [2-5], poly(methylmethacrylate) (PMMA) [3, 6], poly(vinyl chloride) (PVC) [5, 7, 8], poly(ethylene terephthalate) (PET) [3, 7-9], poly(vinylidene fluoride) (PVDF) [10], polystyrene (PS) [11-13], poly(ether ether keton) (PEEK) [14], nylon 6 [8], and poly(amidoamine)s [15]. The X-ray induced sample damage is a common problem during the XPS analysis of materials, and can cause the spectrum to change with the exposure time. From the experimental viewpoint, Buchwalter and Czomyt [6] classified the main chemical changes in polymers in three cases as; (1) main-chain scission, (2) cross-linking, and (3) volatile product formation and cyclization. We think most of the interesting points to such X-ray bombarded polymers are to obtain the information about the electronic states of chemical bond for the polymer in detail from theoretical and experimental analysis.

In a previous work [16], some of us demonstrated the analysis of surface damage for nitrocellulose (NC) and PTFE, by considering thermal effects due to Al Kα X-ray irradiation with an unmonochromated source that the cleavage sites of polymers can be predicted owing to two-center bond energies of the model oligomers from a semi-empirical MO calculation. The valence XPS of NC at the initial time, and after 120 minutes of the irradiation were simulated considerably well by deMon density-functional theory (DFT) program [17] using the model molecules.

In the present work, we analyze experimental valence X-ray photoelectron spectra (XPS) of PVC polymer by X-ray irradiation from the theoretical viewpoint. In the case of X-ray irradiation with the unmonochromated source, the samples are much closer to the X-ray anode, and then thermal effects may be more important. Thus, we will predict the cleavage sites of chemical bond for PVC from two-center bond energies of the model pentamer by a semi-empirical AM1 MO calculation [18]. In the prediction, we assumed that thermal effect is important in Al Kα X-ray

irradiation with an unmonochromated source. We will also simulate experimental valence XPS of the PVC polymer after the initial, 120, and 260 minutes of the irradiation by deMon DFT calculations using the model pentamer.

Experimental

We used commercially available polyvinyl chloride [$(CH_2CHCl)_n$, (PVC) (Aldrich chemical Co. Inc; M_W 83500)].

X-ray photoelectron spectra of the pellet were obtained on a PHI 5400MC ESCA spectrometer, using an unmonochromated Al Ká radiation. The spectrometer was operated at 600 W, 15 kV, and 40mA. Photon energy was 1486.6 eV. A pass energy of 71.55 eV was used for high resolution scans in a valence band analysis (50 eV of range). The angle between the X-ray source and analyzer was fixed at 45°. Dispersion compensation yielded an instrumental resolution of 0.5 eV with full width at half-maximum on the Ag 3d line of silver. Multi-scan averaging on a multi-channel analyzer was used for the valence band region, although a very low photoelectron emission cross-section was observed in this range. The spot size in the measurement was 3×1 mm.[2]

Computational Detail

For the vertical ionization potentials (VIP)s of the valence regions, we use the so-called restricted diffuse ionization (rDI) model. In the case of the ionization of an electron from molecular orbital (MO) ϕ_k of interest, the fraction of electron is removed according to the Janak theorem [19]. In the rDI model, half of an electron is removed evenly from the valence MOs and the negative of the resulting orbital energies correspond to calculated VIPs. This allows us to obtain all valence VIPs in a single calculation.

The intensity of valence XPS was estimated from the relative photo-ionization cross section for Al K á radiation using the Gelius intensity model [20]. For the relative atomic photo-ionization cross-section, we used the theoretical values from Yeh [21]. The model molecule of PVC was calculated by deMon DFT program using model pentamer, H-$(CH_2CHCl)_5$-H. For the geometry of the molecule, we used the optimized cartesian coordinates from the semi-empirical AM1 (version 6) method [18]. DeMon calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional [22] and Perdew's 1986 correlation functional [23]. In the program, we used a nonrandom grid and polarized valence double-ς (DZVP) basis of (621/41/1*) and (6321/521/1*) for C and Cl, and (41) for H with auxiliary fitting functions labeled (4, 4; 4, 4) and (5, 4; 5, 4) for C and Cl, and (3, 1; 3, 1) for H.

In order to calculate each intensity of valence XPS for the model molecule, we considered only the atoms of the model molecule, H-$(CH_2CHCl)_5$-H, in the parenthesis. To simulate the valence XPS of the polymer theoretically, we constructed from a superposition of peaks centered on each VIP, I_k. As was done in previous work [24-26], each peak was represented by a Gaussian curve, and we used the line-widths, $WH(k) = 0.10\ I_k$ (proportional to the ionization energy) for valence XPS.

Results and Discussion

a) Experimental spectra for X-ray irradiated PVC

We think the decomposition process of surface damage with an unmonochromated X-ray source may be very complicated. However, thermal effects may be more important, since the sample is much closer to the X-ray anode. We will, thus, predict where the cleavage of the polymer-bond occurs in X-ray irradiation. When we consider the dissociation of the functional groups in the molecules of the surface due to the thermal effects, we can estimate the cleavage of polymer-bonds from the bond-orders and two-center bond energies of the model molecules by MO calculations using AM1 method, as indicated in our previous works [16, 27, 28]. Here, we will estimate where the cleavage of the PVC occurs from the two-center bond energies of the model pentamer molecule by the semi-empirical MO calculations.

In Fig.1, we showed two-center bond energies of the model pentamer for PVC, by considering the thermal effects from the values of the two-center bond energy. The C-Cl bond energy as 10.8 eV is less than the value (14.3 eV) for the C-C bonds. Thus, the cleavage of C-Cl bonds occurs first in PVC. In PVC, C-Cl bonds will cleave first on the utmost surface, since the value (10.8 eV) of the bond energy is the least. The estimation can result in the scission of C-Cl bonds for PVC due to the X-ray radiation.

The decomposition process of PVC due to X-ray induced surface damage was observed from the X-ray photoelectron valence spectra at the initial time and after 120 and 260 minutes of X-ray irradiation in Fig. 2 ***a***) – ***c***), respectively. The peak (at around 8 eV) of valence spectra lowers gradually after 120 and 260 minutes at an Al Ká X-ray source power of 600 W, in comparison of the intensity with the peak at the initial time. The result corresponds well to the prediction of the scission of C-Cl bonds using MO calculations. As indicated in the previous work [25], the peak at around 8 eV is due to the lone-pair electrons of Cl-3p non-bonding orbitals. In Table 1, we showed the observed peaks, calculated VIPs, main contributions of atomic orbital photo-ionization cross-section, orbital nature, and the functional groups for valence X-ray photoelectron spectra of the PVC. The valence X-ray photoelectron spectra at the initial time, and after 120, and 260 minutes will be analyzed by deMon DFT calculations using model pentamer.

Table 1. Observed peak, VIP, main AO photo-ionization cross-section, orbital nature and functional group for X-ray photoelectron spectra of PVC

observed peak (eV)	VIP (eV)	main AO photo-ionization cross-section	orbital nature	functional group
20.0(18.0-24.0)[a]	19.7-24.9	Cl3s, C2s	{sσ(C2s-Cl3s)-B, sσ(C2s-C2s)-B }	-C-Cl -C-C-
16.0(14.0-17.0)[a]	16. 3-18.2	C2s	{pσ(C2s-C2p)-B, pσ(C2p-Cl3s)-B}	-C-C -C-Cl
shoulder(9.0-13.0)[a]	10.8-14.7	C2p	pσ (C2p-C2p)-B	-C-C
8.0(5.0-9.0)[a]	8.6-9.8	Cl3p	lone-pair(Cl3p)-NB	-Cl

[a] shows the peak range. WD (difference between calculated and observed peaks) = 3.5eV

b) Decomposition mechanism for X-ray irradiated PVC

Let's consider the decomposition process of PVC from analysis of the experimental valence electron spectra by deMon DFT calculations using the model pentamer. The decomposition process of the cleavage for the model pentamer of PVC due to the X-ray irradiation may be written into five steps (*A*) - *E*)) by considering the scission of C-Cl bonds due to the thermal effect. It can be seen from the change of the valence spectra in Fig. 2 ***a***) – ***c***) that the peak due to the Cl-2p electrons (at around 8 eV) lowers gradually after 120 and 260 minutes X-ray irradiation, in comparison of the intensity with the peak at the initial time.

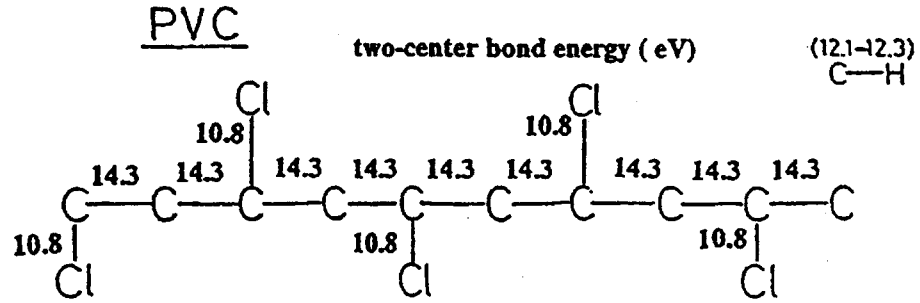


Fig. 1. Two-center bond energies of model pentamer for PVC calculated by the semiempirical AM1 method

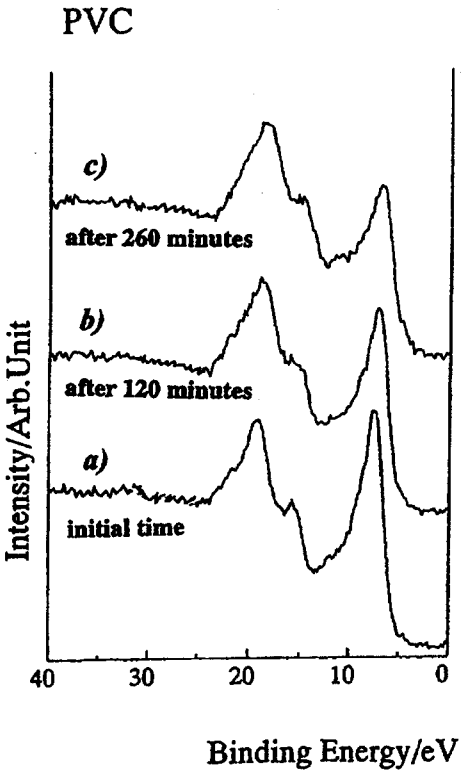


Fig. 2. Observed valence spectra of PVC due to X-ray irradiation at Al Kα X-ray source power of 600 W, *a*) at the initial time, *b*) after 120 minutes, *c*) after 260 minutes

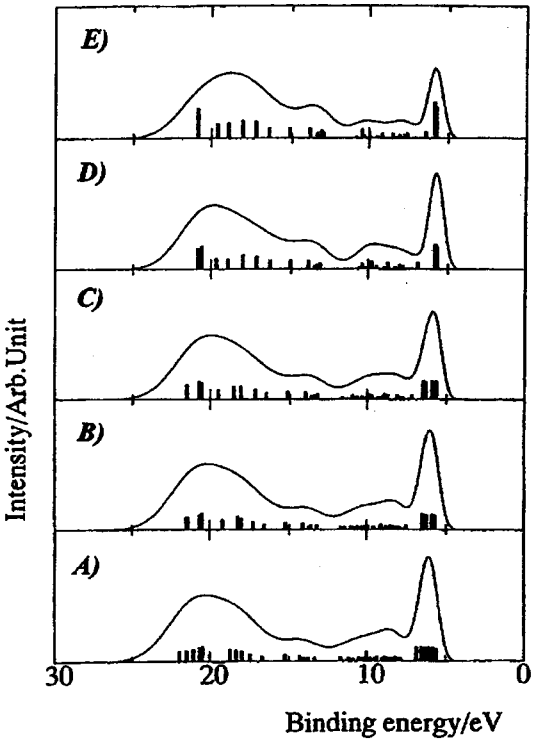
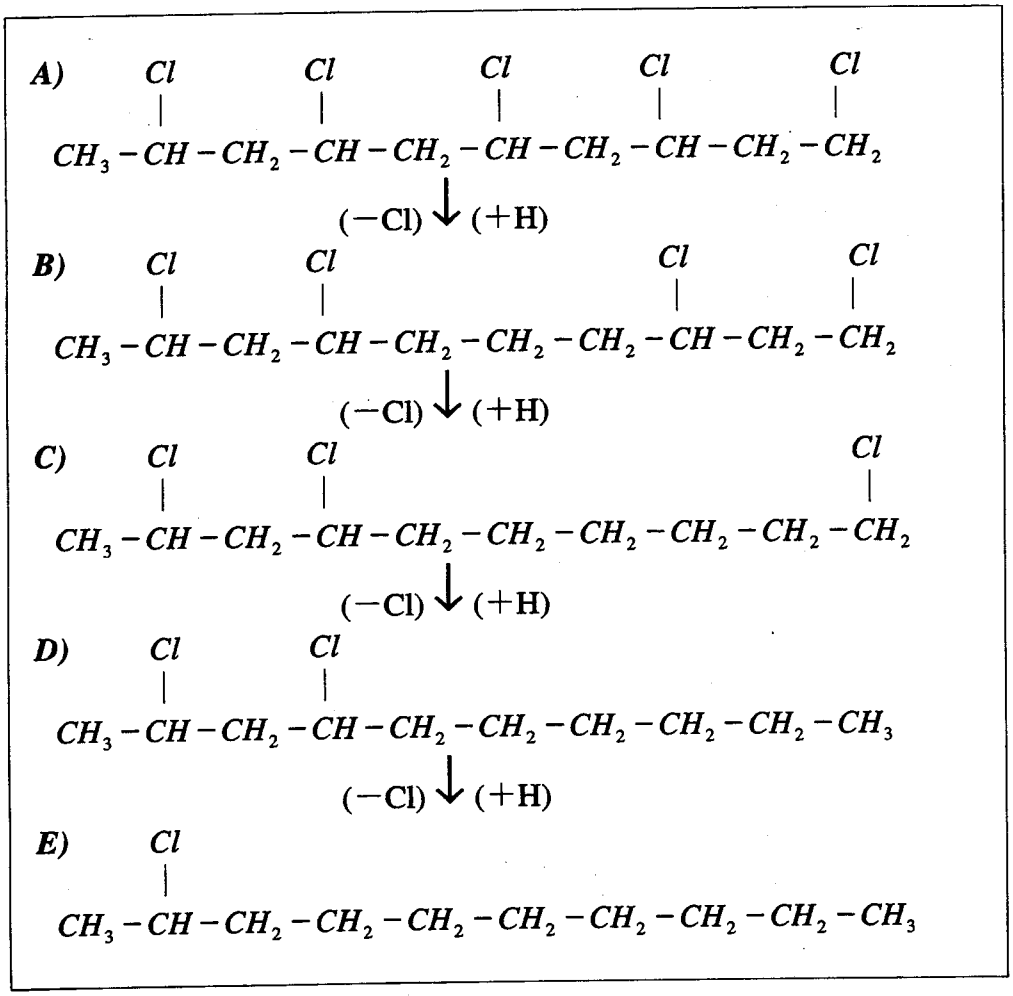


Fig. 3. Simulated valence spectra of PVC due to the pentamer model (*A)* H-$(CH_2CHCl)_5$-H, *B)* H-$(CH_2CHCl)_2(CH_2CH_2)(CH_2CH$-$Cl)_2$-H, *C)* H-$(CH_2CHCl)_2$-$(CH_2CH_2)_2$-$(CH_2CHCl)$-H, *D)* H-$(CH_2CHCl)_2$-$(CH_2$-$CH_2)_3$-H, *E)* H-$(CH_2CHCl)$-$(CH_2CH_2)_4$-H from the bottom) by deMon DFT calculations



Thus, we simulated the pentamer models (*A)* H-$(CH_2CHCl)_5$-H, *B)* H-$(CH_2CHCl)_2$-(CH_2CH_2)-$(CH_2CHCl)_2$-H, *C)* H-$(CH_2CHCl)_2$-$(CH_2CH_2)_2$-(CH_2CHCl)-H, *D)* H-$(CH_2CH$-$Cl)_2$-$(CH_2CH_2)_3$-H, *E)* H-(CH_2CHCl)-$(CH_2CH_2)_4$-H), respectively, in the five steps by deMon DFT calculations. In each step of the decomposition process, we added the H atom by assuming that the H atoms of C-H bond groups cleaves pretty easily and the H atoms may recombine the C atoms in the main chain, since the two-center bond energies are estimated as 12.1-12.3 eV. The results were shown in Fig. 3 ***A)*** - ***E)*** from the bottom.

We omitted the simulation spectra in which the double bond of main chain carbons occurred, because the spectra in the energy range of 15 ~ 30 eV were much broader than the experimental ones in the range of 15 ~ 25 eV.

In order to perform the quantitative analysis due to X-ray irradiation effect for PVC, we estimated the simulated intensity ratio {(peak intensity at around 6.5 eV)/(peak intensity at around 20 eV)} in Fig. 3 ***A)*** − ***E)***, and the experimental ratio {(peak intensity at around 8.0 eV) /(peak intensity at around 20 eV)} in Fig. 2 ***a)*** − ***c)***, respectively. We obtained the theoretical ratios as 1.6, 1.5, 1.3, 1.4 and 1.1 in Fig. 3 ***A)*** - ***E***, while did the experimental ratios as 1.6, 1.3 and 1.1 in Fig. 2 ***a)*** - ***c)***, respectively. We can, thus, conclude that the simulated spectra in ***A)***, ***C)***, and ***E)*** in Fig. 3 correspond well to observed ones in ***a)*** (at the initial time), ***b)*** (after 60 minute), and ***c)*** (after 120 minute) in Fig. 2, respectively.

Conclusions

We performed the surface analysis of PVC polymer due to the X-ray irradiation from the theoretical and experimental valence X-ray photoelectron spectra (XPS).

(1) In order to analyze the decomposition

process of PVC, we estimated where the cleavage of the PVC occurs from two-center bond energy by the semi-empirical MO calculations using the model pentamer. The C-Cl bond energy as 10.8 eV is less than the value (14.3 eV) for the C-C bonds. Thus, the cleavage of C-Cl bonds occurs first in PVC.

(2) We simulated valence spectra by deMon DFT calculations using the pentamer models {***A)*** H-$(CH_2CHCl)_5$-H, ***B)*** H-$(CH_2CHCl)_2$-(CH_2CH_2)-$(CH_2CHCl)_2$-H, ***C)*** H-$(CH_2CH$-$Cl)_2$-$(CH_2CH_2)_2$-(CH_2CHCl)-H, ***D)*** H-$(CH_2$ $CHCl)_2$-$(CH_2CH_2)_3$-H, ***E)*** H-$(CH_2CH$-Cl)-$(CH_2CH_2)_4$-H}, respectively, in Fig. 3, in comparison of the experimental valence spectra at the initial time and after 60 and 120 minutes of X-ray irradiation in Fig. 2. The simulated spectra in Fig. 3 ***A)***, ***C)***, and ***E)*** correspond well to observed ones in Fig. 2 ***a)***, ***b)***, and ***c)***, respectively.

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